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Multipolar ordering in f-electron systems

Summary of the Ph.D. Thesis

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Introduction

Orbital ordering phenomena in f-electron systems have been extensively studied in the past two decades. The highly degenerate f-shells of rare earth and actinide ions support a great variety of local degrees of freedom: magnetic, quadrupolar and octupolar at least. This leads to variegated and complex phase diagrams and magnetic properties. In earlier studies, orbital ordering meant just quadrupolar ordering, but it has become clear that orderings of higher multipoles are also realized in some f-electron compounds. Recent experimental observations on NpO_2 indicate that the primary order parameter of the 25K phase transition is purely octupole. Quadrupolar ordering was found to explain the properties of many Ce, Tm and Pr-based rare earth compounds. However, the physics of multipolar orderings is far from being fully explored yet.

One may think that higher order multipoles are irrelevant because their interaction is much weaker than ordinary dipolar interaction. This seems to be suggested by the multipole expansion in classical electrodynamics. This is, however, misleading. The leading interaction term between the multipoles has quantum mechanical origin, it is mediated by electrons in wide bands like the usual exchange interaction, thus the interactions between multipoles with different rank are equally important.

Many f-electron systems order magnetically. However, quite a few f-electron systems have phase transitions which are thermodynamically as strong as the magnetic transitions, but the low temperature phase is not magnetically ordered. In these cases, we associate the phase transition with the ordering of a multipolar moment. Often it is called "hidden order" because, in contrast to magnetic order, which is easy to detect, multipolar order is not easily seen. Therefore, theoretical investigations of the behavior of multipolar models and the consequences for the magnetic properties are important.

Objectives

The theory of multipolar orderings is a new field. The Hilbert space of local order parameters is multidimensional, the interactions are quite complicated, therefore even the mean field behavior is still largely unexplored. A systematic treatment has to rely on exploiting the symmetries of the system.

One of my objectives was to develop a general scheme for the symmetry classification of the order parameters which can arise for a given set of ionic states. From this, one should be able to derive the general form of the Landau free energy which governs phase transitions. Of particular interest is the effect of magnetic fields which couple the multipolar moments in a manner which depends sensitively on field direction. I used group theoretical arguments.

My second main objective was to understand the nature of the order parameter, and the mechanism of ordering, for several f-electron systems of considerable current interest. In particular, I wished to at least partly explain the following phenomena

- magnetic field effects on the antiferro-quadrupolar ordering transition of $PrFe_4P_{12}$
- the reason for the choice of the octupolar order parameter of NpO_2, and the mechanism of the suppression of octupolar order by magnetic field
- the nature of the so-called hidden order in URu_2Si_2

I summarize the main new scientific results of my Ph.D. work in the next thesis points.

New scientific results

1. I discussed the nature of the field-induced coupling of multipolar degrees of freedom for a number of local symmetries and level schemes [1], [2]. The analysis was carried out in two complementary ways. In one of the schemes, I write down the Landau expansion of the Helmholtz potential which gives the magnetic field as a derived quantity. The invariants used in this expansion are formed according to the zero-field definition of the multipolar moments, and coupled modes are found in terms which transform like the field [2]. The alternative scheme starts with the identification of the reduced symmetry of the system in a magnetic field. In the resulting new symmetry classification, certain multipoles are found to possess the same symmetry and consequently they will appear mixed [1].

2. I pointed it out that Γ_5 octupoles defined on a Γ_8 local Hilbert space possess a single-ion anisotropy which makes the (111)-type orientation of the octupoles preferable [2]. This explains also that the order parameters of NpO_2 are (111)-type Γ_5 octupoles. I showed that the primary octupolar order induces a Γ_5-type quadrupolar order. I determined the phase diagram in the temperature-quadrupolar coupling plane and found that the regime of first-order transitions is bounded by two tricritical points.

3. Motivated by the observation of octupolar order in NpO_2, I introduced a ferro-octupolar lattice model of Γ_8 ions [2]. I discussed the effect of applying an external magnetic field. I found that for certain high-symmetry directions, spontaneous symmetry breaking by octupolar ordering remains possible up to a critical magnetic field. For general field directions, the phase transition becomes smeared out in arbitrarily weak fields.

4. I proposed a new model for the so-called hidden order of URu_2Si_2 [1]. The model is based on a novel crystal field scheme. I classified the possible order parameters and found that induced-moment $\mathcal{T}_z^\beta$ octupolar order is the best choice for the zero-field order. According to this interpretation, hidden order is time reversal invariance breaking without magnetic moments. This explains the result of a crucial recent experiment according to which strain applied in the (100) direction induces large-amplitude antiferromagnetism on the background of the non-magnetic hidden order.

   Furthermore, I discussed the phase diagram up to high magnetic fields. I found a high-field quadrupolar phase disjoint from the low-field octupolar phase. The overall appearance of the phase diagram corresponds to the results of recent high-field experiments.

5. I introduced a new crystal field scheme, the Γ_1–Γ_4 quasiquartet model to describe the magnetic properties and the phase diagram of the $PrFe_4P_{12}$ skutterudite [3], [4]. In this model, inter-site interactions induce the Γ_3 quadrupolar moments which undergo antiferro-quadrupolar ordering. I found that, with allowing also for dipolar interactions, the model gives a good description of the susceptibility, the field dependence of the specific heat, and the metamagnetic transition. I derived the phase diagram in the temperature–magnetic field plane, and found a tricritical point separating the regimes of low-field second order, and high-field first order transitions.

6. I suggested a possible interpretation of the strong magnetic non-linearity observed in $PrBa_2Cu_3O_6$ [3]. Using the standard quasi-triplet crystal field model, I studied the interplay of quadrupolar and dipolar interactions. I found that quadrupolar interactions can assist magnetic ordering, which is possibly related to the anomalously high Néel temperature of $PrBa_2Cu_3O_6$. I discussed the mean-field theory of the phase transitions of the model. For magnetic field directions in the tetragonal *ab*

plane, I derived the following results: (i) the linear susceptibility turns upwards at the quadrupolar ordering transition; (ii) there is a large peak of the non-linear susceptibility χ_3; (iii) the transition is smeared out in strong fields.

7. I discussed the general relationship between magnetic anomalies observed at a critical temperature of a non-magnetic ordering transition, such as the quadrupolar and octupolar transitions described in my Ph.D. thesis. The Ehrenfest equation connecting the discontinuity of the temperature derivative of the linear susceptibility with the discontinuity of the non-linear susceptibility can be continued to the tricritical point. The tricritical limiting behavior can be of two different kinds, and both can be realized by tuning one of the parameters of our quadrupolar–octupolar model [2].

Publications related to the Ph.D. work

[1] A. Kiss and P. Fazekas
Low-field octupoles and high-field quadrupoles in URu_2Si_2
cond-mat/0404099, submitted for publication to Phys. Rev. (2004)

[2] A. Kiss and P. Fazekas
Octupolar ordering of Γ_8 *ions in magnetic field*
Phys. Rev. B **68** 174425 (16 pages) (2003)

[3] A. Kiss and P. Fazekas
Quadrupolar interactions in Pr compounds: $PrFe_4P_{12}$ *and* $PrBa_2Cu_3O_6$
Journal of Physics: Condensed Matter **15** S2109-S2117 (2003)

[4] P. Fazekas and A. Kiss
Competition and coexistence of magnetic and quadrupolar ordering
NATO SCIENCE SERIES: II: Mathematics, Physics and Chemistry 110 "Concepts in Electron Correlation" edited by Alex C. Hewson and Veljko Zlatic, 169-177 (2002)